Trends in Heavy Fermion Matter

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Abstract.

A brief review on major advances in heavy fermion physics is presented including the Ce metal phase diagram, the huge effective mass detected in $CeAl_3$, and the successive discoveries of unconventional superconductivity in $CeCu_2Si_2$ and three U based compounds, UBe_{13}, UPt_3 and URu_2Si_2. In order to track the origin of the huge effective mass, the case of intermediate valence compounds is discussed with emphasis of the differences between Yb and Ce materials. The formation of the effective mass is analyzed by two regular- and singular-part contributions. Examples are given for both, antiferromagnetic ($CeRu_2Si_2$ series) and ferromagnetic tricriticalities (UGe_2). Pressure and magnetic-field studies on the ferromagnetic superconductor URhGe illustrate the role of the singular effective mass enhancement on the superconducting pairing. The discovery of the Ce-115 material gives the opportunity to study deeply the interplay of antiferromagnetism and superconductivity. This is clearly demonstrated by field re-entrance AF inside the SC phase just below the superconducting upper critical field (H_{c2}) for $CeCoIn_5$ or on both side of H_{c2} within a restricted pressure window for $CeRhIn_5$. The present status of the search for the hidden-order parameter of URu_2Si_2 is given and we emphasize that it may correspond to a lattice unit-cell doubling which leads to a drastic change in the band structure and spin dynamic, with the possibility of competition between multipolar ordering and antiferromagnetism.

1. Introduction

Heavy fermion compounds (HFC) are of special interest as a large variety of ground states can be achieved and a strong interplay between them occurs. Due to the weakness of their corresponding characteristic temperature a change from one state to another can be easily realized by moderated temperature (T), pressure (P), or magnetic field (H) tunings. Heavy-fermion quasiparticles are the result of strong magnetic and valence fluctuations.

Heavy fermion physics started with the discovery of the Ce metal phase diagram in which the occupation number (n_f) of the 4f trivalent Ce^{3+} configuration is a key parameter [1]. A boost in the field was the discovery in $CeAl_3$ [2] that even with n_f close to unity the establishment of long range magnetic ordering can be avoided with the benefit of the formation of huge heavy quasiparticles. The Sommerfeld coefficient $\gamma \sim 1\,\mathrm{J\,mole^{-1}K^{-2}}$ surpasses that of a free electron value by three order of magnitude. The description from single Kondo impurity to a regular array of Kondo centers (the Kondo lattice) is still the subject of debate [3]. At least, now it is well established that heavy quasiparticles move along the trajectories of the Fermi Surface [4, 5].

A major breakthrough was the discovery of superconductivity (SC) in $CeCu_2Si_2$ [6] which opened the era of unconventional SC. This new research field was reinforced by the concomitant discoveries of SC in three uranium HFC namely UBe_{13} [7], UPt_3 [8], and URu_2Si_2 [9, 10]. Unconventional SC with a sign-reversing order parameter (OP) was directly proved by the observation of multiple SC phases in UPt_3 [11]. New features of unconventional SC, e.g. the unitary treatment of impurities [12, 13], were rapidly derived from HFC studies [14, 15], whereas it took, for instance, a decade before serious considerations of unconventional SC were put forward in organic conductors.

The achievement of huge effective mass was rapidly related to the proximity to a magnetic instability, but it took over a decade before the advent of quantitative studies focusing on quantum criticality such as the switch from paramagnetic (PM) to antiferromagnetic (AF) ground states. Since this point is highly discussed by other authors [16, 17], we will focus here on different facets of HFC going from the main discoveries to the present status.

In this article special attention is given to: (i) the (H, P, T) phase diagram ranging from intermediate valence compounds to examples of tricriticality for both antiferromagnetic (AF) and ferromagnetic (FM) materials, (ii) recent investigations on the interplay between effective mass enhancement and SC, and (iii) the resolution of the puzzle of the hidden order (HO) phase of URu_2Si_2.

2. Intermediate valence compounds

De facto, HFC belongs to the general class of the anomalous 4f or 5f compounds These were recognized six decades ago via the discovery of the high pressure phase diagram of Ce metal (Fig. 1). The first order transition at $T_{\gamma\alpha}$ from a PM γ phase to a PM

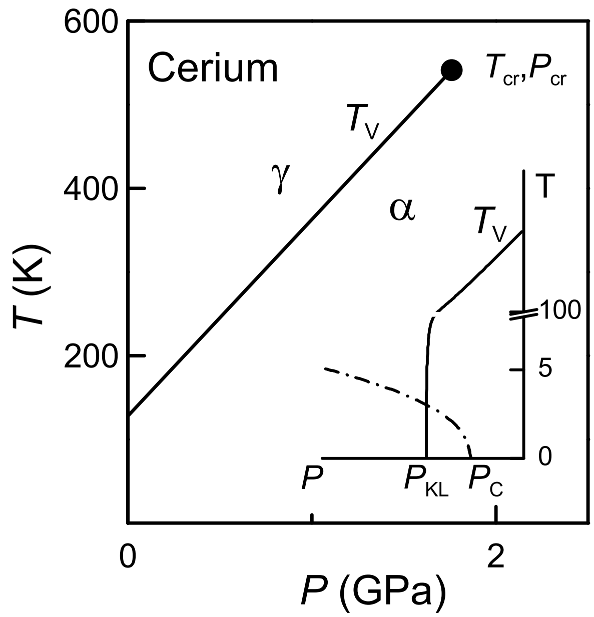

Figure 1. Pressure-temperature phase diagram of Ce metal (T, P) with the first order transition $T_V(P)$ between the γ and the α phase and its critical end point. If the volume can be expanded: (i) $T_V(P)$ will collapse abruptly at $T = 0\,\mathrm{K}$ for $P = P_{KL}$ and (ii) magnetic ordering (dashed dotted line) will collapse at the critical pressure P_c[18]

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α phase is isostructural. It ends up at a critical end point (CEP) at $T_{cr} \sim 600\,\mathrm{K}$ and $P_{cr} \sim 2\,\mathrm{GPa}$. From high energy spectroscopy, n_f in the γ phase is near unity while even in the α phase n_f remains high ($n_f \sim 0.9$). Thus the transition at $T_{\gamma\alpha}$ is connected to an abrupt change in the valence and $T_{\gamma\alpha} = T_V$ the temperature of the valence transition. At ambient pressure, $T_V(0) \sim 100\,\mathrm{K}$, such a high value prevents the establishment of long range magnetic ordering. However, if $T_{\gamma\alpha}$ collapses we must consider on equal footing the interplay of valence and magnetic instability [18]. If a negative pressure could be realized, AF for example would appear below a Néel temperature (T_N) up to a pressure P_c. An interesting problem is the consequence of an intercept between the valence transition line ($T_V(P)$) which must collapse at some pressure P_{KL} at $T \to 0\,\mathrm{K}$ and the AF–PM boundary. Thus in addition to the magnetic instability at P_c a possible Fermi surface instability may occur. Furthermore, if T_V becomes comparable to any characteristic temperature of a specific bare ground state like T_N for AF, T_{Curie} for FM, or T_{SC} for SC, the valence transition or its fluctuations near its CEP must be considered in addition to the spin fluctuations. The interplay between the different phase diagram reported Fig. 2 may lead to new coexisting matter such as the AF + SC phase of $CeRhIn_5$ discussed later. A discussion on valence fluctuations is given in the contribution of K. Miyake [19]. Strikingly, a first order valence transition similar to that in Ce metal has almost never been observed in any Ce HFC. The main reason is that the repulsion term U_{fc} between the 4f electron and the light electron plays a critical role

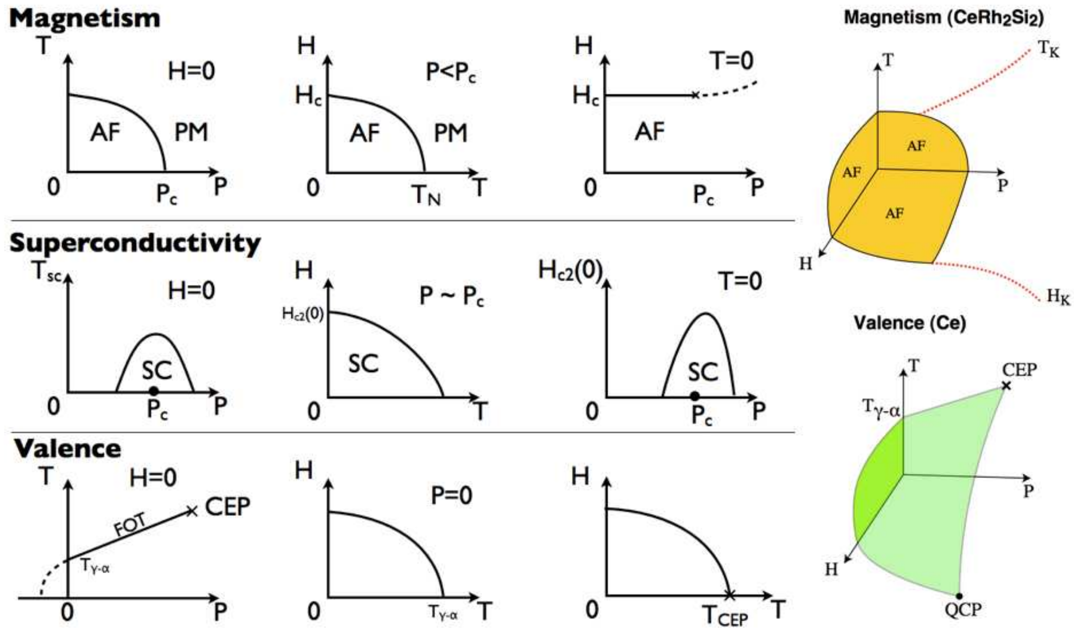


Figure 2. Interplay between (H, T, P) phase diagram for the magnetic, superconducting and valence transition. H re-entrance of AF results from the interplay between magnetic and superconducting phase diagram; in Yb HFC, our guess is that there is a strong interplay between magnetic and valence phase diagram[21].

in controlling the position of the zero temperature CEP as a function of the relative ε_f of the 4f level with respect to the Fermi level [20]. Thus, very often the valence fluctuations can only be felt and the precise location of the valence quantum critical point is a "ghost" centered around $P = P_{\rm V}$ but will react to magnetic field sweeps. For Ce HFC, there are clear examples, e.g. $CeCu_2Si_2$ or $CeRu_2Si_2$, where $P_{\rm c}$ and $P_{\rm V}$ are well separated ($P_{\rm V} - P_{\rm c} \sim 4\,$GPa) but in most cases $P_{\rm c} \sim P_{\rm V}$. Furthermore $P_{\rm V}$ coincides with the crossover pressure $P^*_{\rm CF}$ where the Kondo energy $k_{\rm B}T_{\rm K}$ surpasses the crystal field splitting $C_{\rm CF}$ and the full degeneracy $2J + 1$ of the 4f level is recovered [21].

Often the trivalent Yb ions with 13 4f electrons are considered as the 4f hole analog of trivalent Ce. However, we want to point out two major differences [21, 22]: (i) the deeper localization of the 4f electron of Yb with respect to Ce implies that the width Δ of the 4f virtual band states is one order of magnitude smaller in Yb HFC than in Ce HFC, (ii) the larger strength of the spin-orbit coupling λ between the $j = l - 1/2$ and $j = l + 1/2$ individual configuration of the angular momentum $l = 3$ for Yb than Ce. This leads to the hierarchy $\Delta > \lambda > C_{\rm CF}$ for Ce and $\lambda > \Delta \sim C_{\rm CF}$ for Yb. Consequently, in Ce HFC, the variation of n_f is restricted between 1 to 0.84. Contrary, for Yb centers, n_f can vary from 0 to 1 i.e. with a valence changing from 2 to 3. These hand waiving arguments are clearly illustrated in band structure calculations (for example see in ref.[22] the contrast between $CeRh_2Si_2$ and $YbRh_2Si_2$).

Another difference is that the pressure $P^*_{\rm CF}$ can be located deep inside the intermediate valence phase (Fig. 3) as pointed out two decades ago for the analysis of

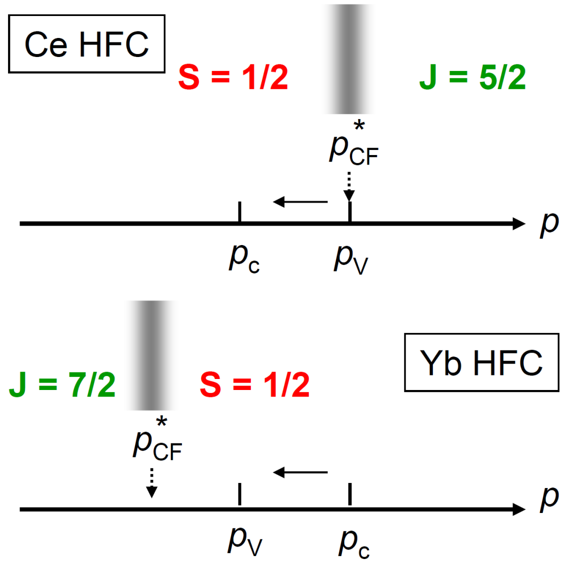


Figure 3. Schematic difference between Ce and Yb HFC on the hierarchy between their characteristic pressure for the crystal field wipe out (P^*_{CF}); for the valence transition (P_{V}) and for the magnetic instability (P_{c})[21].

Mössbauer experiments on $YbCu_2Si_2$ [23] and experimentally observed for $YbInCu_4$ [24]. The latter compound represents a beautiful example of a first order valence transition with the strong interplay between valence and magnetic fluctuations (Fig. 4). In agreement with recent theoretical developments [19] we want to stress that at least for Yb HFC the interplay between valence and magnetic fluctuations is strong. A nice

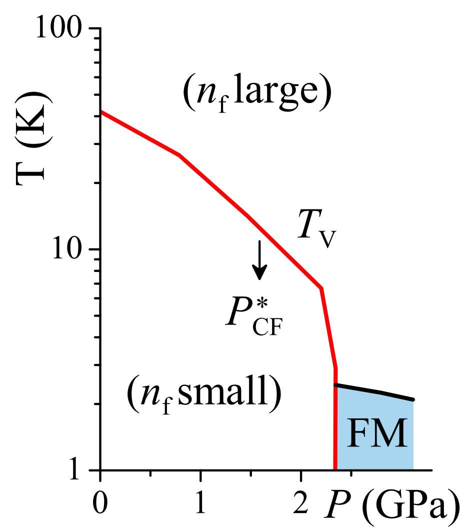


Figure 4. Schematic (T, P) phase diagram of $YbInCu_4$. T_{V} has been determined by resistivity and NQR, T_{Curie} by susceptibility and NQR. P^*_{CF} indicates the crossover pressure for the mergence of crystal field effects[21, 24]

illustration for this is the work on β-$YbAlB_4$ [25] presented by S. Nakatsuji at this conference.

Before discussing the formation of the huge effective mass, let us stress that the metal-insulator transition, which can occur in anomalous rare earth compounds, remains a quite puzzling problem. Four decades ago, systems like SmS [26], SmB_6 [27], YbB_{12} [28], where the valence mixing is directly linked to the formation of an extra carrier via a relation like $Sm^{2+} \leftrightarrow Sm^{3+}$ + 5d, surprisingly end up in an insulating ground state, despite the fact that the occupation number of the divalent configuration $1 - n_f$ is only about 0.3. Paradoxically, the low temperature properties seem to be renormalized to the divalent non-magnetic state even if the occupation number of the trivalent configuration $n_f = 0.7$ is higher than the divalent one. New sets of experiments for SmS [29, 30] and SmB_6 [31] have clearly shown (Fig. 5) that this unconventional insulating phase is rather robust, but the ground states changes through a first order transition to a metallic long range ordered magnetic phase under pressure when n_f approaches closely to unity. We believe that these new data require new theoretical insights as well as a better understanding on their differences with the examples of so-called Kondo insulators such as CeNiSn [32] and $CeRu_4Sn_6$ [33].

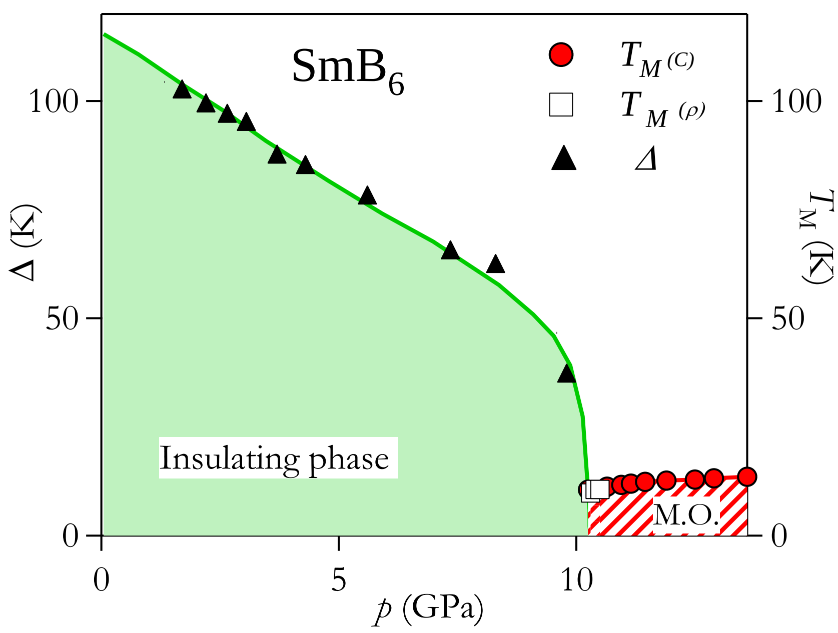


Figure 5. (T, P) phase diagram of SmB_6. At low pressure, the ground state is PM and insulating. Above $P \sim 10$ GPa, it switches to metallic and long range magnetic ordered through a first order transition [31].

3. Origin of heavy fermion quasiparticle

The huge effective mass $m^* \sim 100\, m_0$ is the result of two additional effects: (i) the renormalization of the bare band mass m_B and (ii) an additional contribution m^{**} due

to the development of magnetic or valence correlation. Thus $m^* = m_B + m^{**}$. The last term m^{**} is directly linked to the possible occurrence of unconventional SC. In the strong coupling theory of SC the coupling constant λ is equal to m^{**}/m_B. However, fits to the temperature dependence of the superconducting upper critical field $H_{c2}(T)$ indicates that λ usually never reaches a very high value and even near a magnetic quantum critical point $(1 < \lambda < 2)$ [34]. Thus, a large part of the effective mass enhancement comes from the renormalization of the band mass m_B.

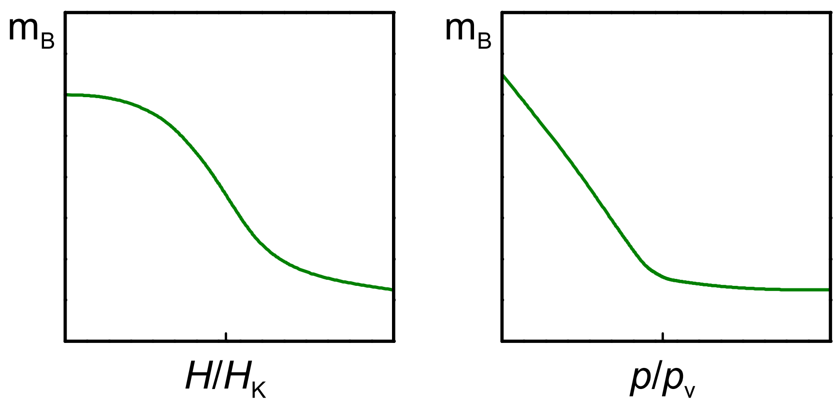


Figure 6. Schematic representations of the field and pressure variation of the regular renormalized band effective mass.

Figure 6 mimics the H and P variation of the regular part (m_B) in a scheme where the renormalized band mass m_B will be mainly given by local Kondo fluctuations. Thus m_B will depend on the strength of the Zeeman energy in comparison to the Kondo energy leading to a crossover field $H_K \sim k_B T_K / g\mu_B$ and on the proximity to the valence transition (P_V). Magnetic fields can induce rapidly a strong magnetic polarization (often 10 % in a field of 10 T) that can decouple spin up and spin down sub-bands with different Fermi wave vector ($k_{F\uparrow}$, $k_{F\downarrow}$) and effective masses. In the frame of global criticality, it is assumed that the regular part m_B has a weaker H and P dependence than the singular part m^{**} close to the quantum singularity.

Figure 7 represents the qualitative P and H dependence of the dynamical susceptibility of an AF system at its hot spot at Q and the corresponding variation of m^{**}_Q of an antiferromagnet which goes from an AF to PM phase through a metamagnetic transition. As shown below for $CeRu_2Si_2$, for $P > P_c$ the metamagnetic field H_c is replaced by pseudo-metamagnetic phenomena at H_M which can be considered as a continuation of the metamagnetic critical end point H^*_c. Furthermore, the induced magnetization leads to the development of FM fluctuations that originate from the AF correlations with enhanced fluctuations at H_c or H_M. Hence an extra contribution of m^* (m^{**}_Q) will appear in magnetic field. It has been recently demonstrated that for AF systems both singular contributions m^{**}_Q and m^{**}_0 are comparable close to P_c [35].

Before discussing in more detail tricriticality phenomena for two selected examples, the $CeRu_2Si_2$ series (AF) and of UGe_2 (FM), we point out that there is no consensus

about the possibility of a divergence of m^* in HFC. For the global scenario often referred to as the conventional spin-fluctuation approach [36], there is no divergence of m_Q^{**} at the AF singularity, even for a second order quantum critical point. For FM material a possible divergence of m_0^{**} at the FM quantum critical point is totally wiped out by the first-order nature of the singularity [37]. In the local quantum criticality scenario, a divergence of effective mass is often invoked at its magnetic quantum critical field notably for $YbRh_2Si_2$ H_C [38, 39]. We consider there is no evidence of such a divergence [22]. Effectively a maximum of m^* occurs at H_c with a very sharp decrease of m^* for $H > H_c$. This situation is quite comparable to that of the polarized phase of $CeRu_2Si_2$ which is discussed hereafter and in contrast with a smooth H increase of m^* going from $H = 0$ to $H = H_c$. It is obvious that a new set of experiments is required to settle this point. Possible candidates to study are cage compounds like the recently investigated YbT_2Zn_{20} systems [40, 41]. In these system a γ term as large as $10\,\mathrm{J\,mole^{-1}K^{-2}}$ has been reported with strong magnetic field effects and they open new possibilities to study the formation of the effective mass.

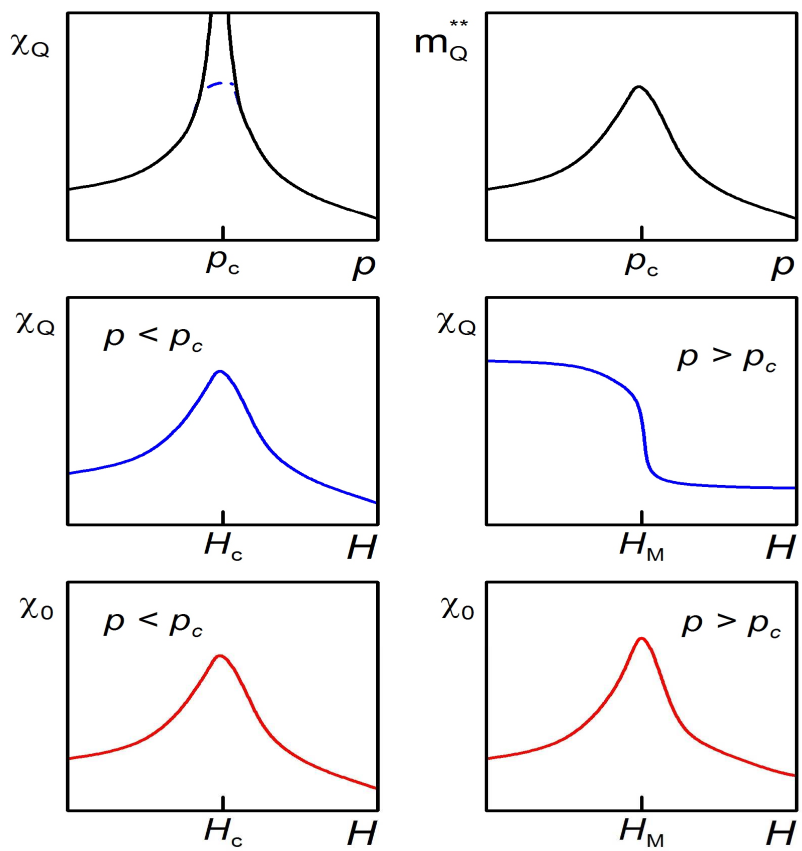


Figure 7. H and P variation of the two singular (AF and FM) part contribution of m^*: m_Q^{**} and m_0^*.

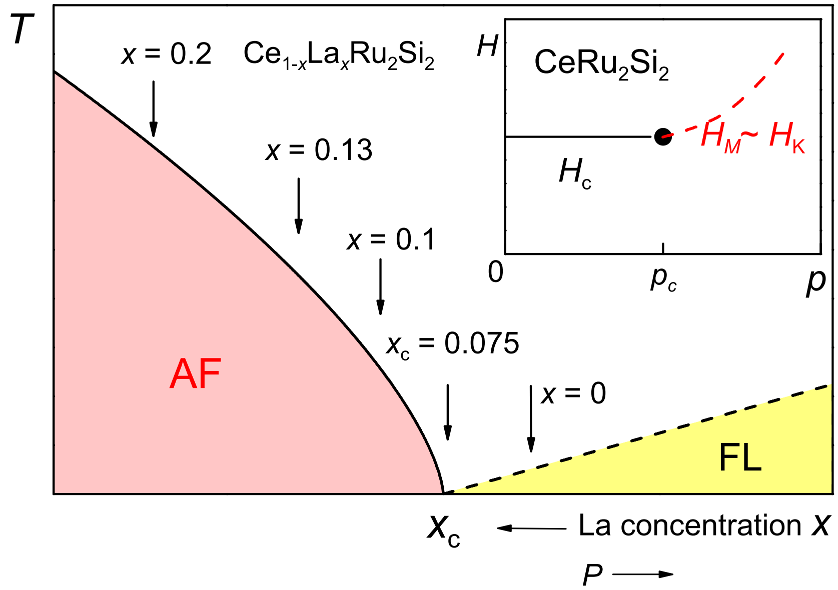


Figure 8. Magnetic phase diagram of $Ce_{1-x}La_xRu_2Si_2$ as function of the La concentration x. The inset shows for $CeRu_2Si_2$ the evolution of the metamagnetic field H_c as function of pressure. H_c ends at the metamagnetic critical field end points H_c^*. Just above the quantum critical point, the metamagnetic phenomena is replaced by a sharp pseudo-metamagnetic crossover at H_M[18].

4. Tricriticality: the AF $CeRu_2Si_2$ series — the FM UGe_2 case

$CeRu_2Si_2$ has been highly studied as it is located close to the AF instability on the PM side ($P_c \sim -0.3$ GPa). It is also one of the few HFC where the Fermi surface is fully determined [42] and thus allows a real proof on the itinerant 4f electron description. Furthermore, extensive inelastic neutron experiments show that the AF correlations develop up to $T_{corr} = 60$ K i. e. at temperature higher than the single Kondo temperature $T_K \sim 25$ K [43]. Clearly, there is no evidence of an intermediate temperature regime where the effective mass enhancement will be dominated by m_B. This is well demonstrated by the continuous increase of the electronic Grüneisen parameter ($\Omega(T)$) on cooling [44, 45] since if, in a finite T range, the free energy will be controlled by a main parameter T^*, a constant Grüneisen regime must emerge. The large value of the ratio T_{corr}/T_K agrees with the conclusion that in HFC the 4f centers behave as single site Kondo centers only at high temperatures [46].

Expanding the lattice volume of the $CeRu_2Si_2$ by La doping, induces AF order above a critical doping level (x_c) near 7 % La (Fig. 8). The Ising character of the localized spin leads to clear first order metamagnetic phenomena at a field $H_c \sim 4$ T. The value of H_c is weakly pressure dependent leading to a critical end point at ~ 4 T for $P = P_c$ on $x = x_c$. Entering in the PM regime above P_c, the metamagnetic transition ($P < P_c$, $H = H_c$) changes to sharp pseudo-metamagnetic crossover at a field H_M. Furthermore the characteristic field H_c, or H_M, corresponds to a critical value $M_c \sim 0.4\,\mu_B$ of the

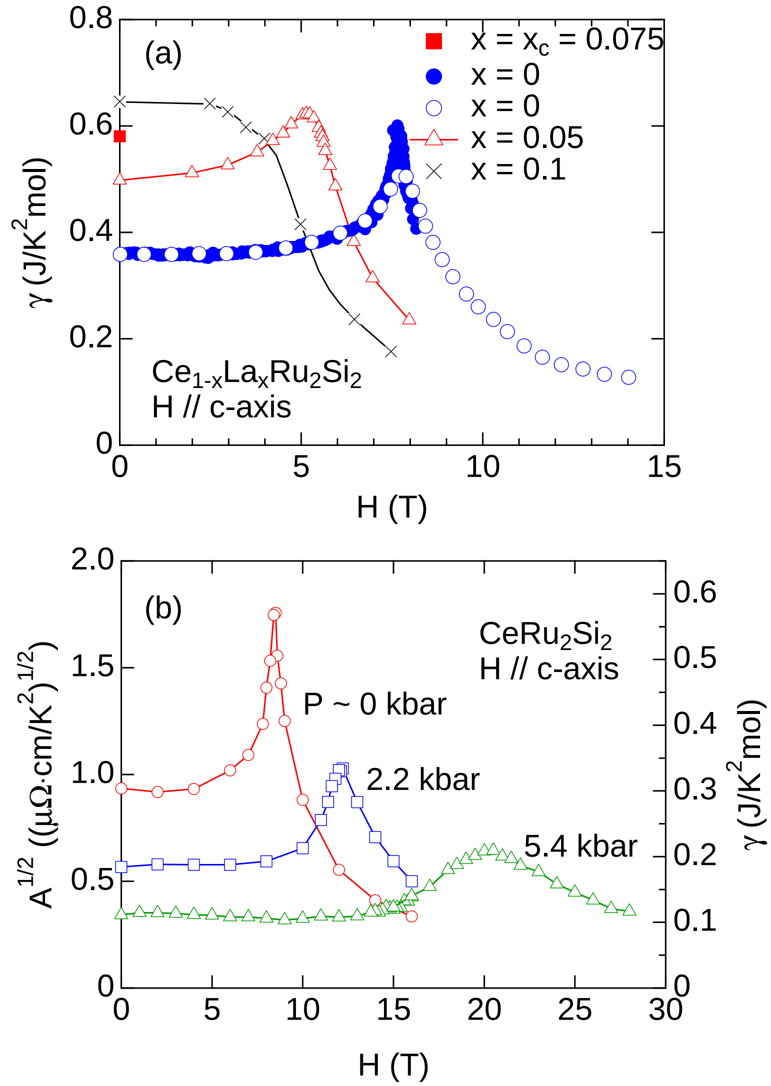


Figure 9. (a) Field variation of the Sommerfeld coefficient of $Ce_{1-x}La_xRu_2Si_2$ for $x = 0$, $x = 0.05$ which is on the AF side ($x < x_c \sim 0.075$), and $x = 0.1$ which are located on the paramagnetic side. At H_c or H_M close to P_c, $\gamma(P_c)$ i. e. the value at x_c is almost the values at H_c or H_M ($\gamma(H_c\,\mathrm{or}\,H_M)$) [51]. Lower panel (b) shows the variation of $\gamma(H)$ at ambient pressure compared to the field dependence of $\sqrt{A}$ under pressure recently deduced from resistivity experiments [50].

magnetization. This points out that the increase of the volume of the majority spin band is the source of the metamagnetic and pseudo-metamagnetic phenomena. Microscopic inelastic neutron scattering experiments show [47, 48] that, for $CeRu_2Si_2$, a drastic softening of the FM fluctuation occurs at H_M while the intensity of the AF correlation collapses at H_M with almost a persistence of the same energy for the AF fluctuation itself [49]. It was recently stressed [50, 51] that close to P_c a quasi-convergence between the effective mass m^* (H_c or H_M) at H_c or H_M and the effective mass $m^*(P_c\ )$ at P_c in zero magnetic field exists: $m^*(P_c) \sim m^*(H_c)$ as illustrated in Fig. 9. For $x = 0.1$

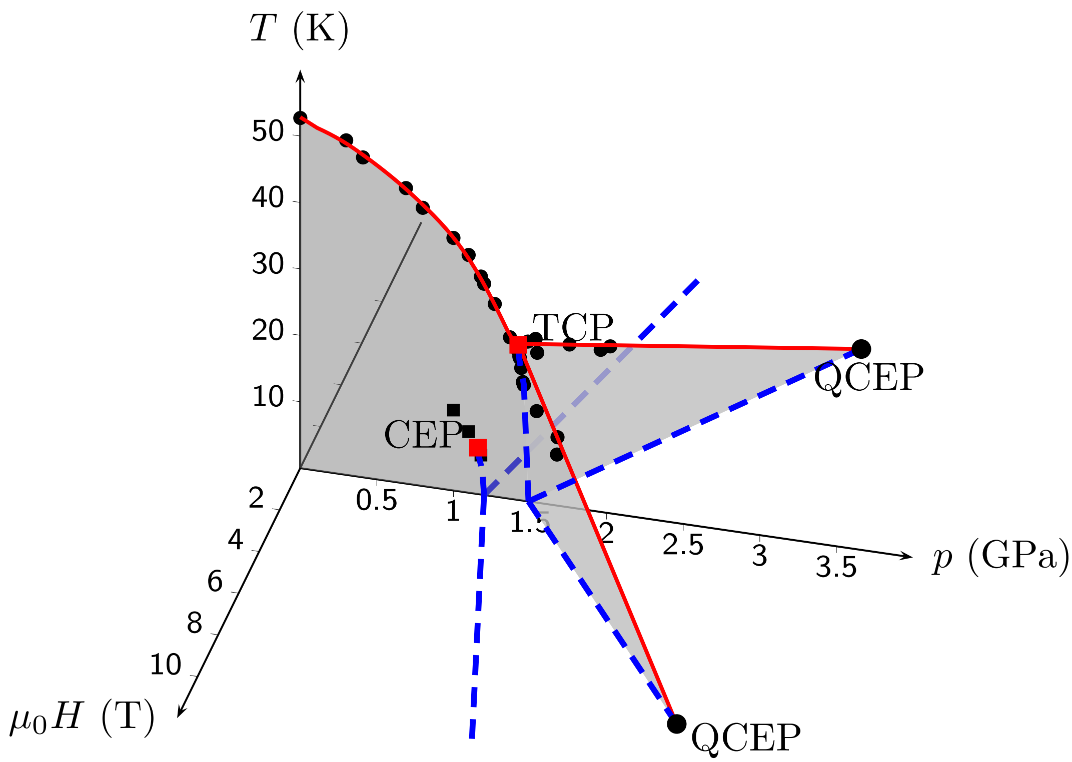


Figure 10. UGe_2 wings with the tricritical pressure P_c at $T = 0\,K$ and the collapse of the first order metamagnetic transition at $T = 0$ for $P_{QCP} > 3\,GPa$ and $H_{QCP} > 16\,T$[54]

with a Néel temperature $T_N \approx 4\,K$ the Sommerfeld coefficient at $H = 0$ is about $\gamma = 0.65\,J\,mole^{-1}K^{-2}$ and decreases monotonously with increasing field. At the critical point $x_c \sim 0.075$ we find $\gamma \approx 0.6\,J\,mole^{-1}K^{-2}$, quite similar to value for $CeRu_2Si_2$ at H_M. Escaping further from P_c by applying a pressure on $CeRu_2Si_2$, the γ term at $H = 0$ decreases strongly in good agreement with the large magnitude of the Grüneisen parameter $\Omega(0) \sim +200$. The relative enhancement of $\gamma(H_M)/\gamma(H = 0)$ is at least at low pressure weakly pressure dependent [50, 51]. Under pressure, correlations are still efficient but form a quite smoother pseudogap than the one built at $P = 0$; the FM interaction is created as the spin up and spin down sub-bands decouple when a critical value of the magnetization is reached [18]. Approaching the valence fluctuation regime, near $P = 4\,GPa$, such a picture will certainly fail. It is worthwhile to point out that in the research on quantum criticality in HFC, most of the results are concentrated on the PM side ($P > P_c$ for Ce HFC); in Grenoble attempts are made now to look more carefully to the AF side ($P < P_c$) and thus to make quantitative comparisons with the recent developments on tricriticality.

It is well known that a FM state can be induced by magnetic field at H_c through a first order transition from a PM ground state at a pressure P higher than the critical pressure P_c of the FM–PM instability at $H = 0$ [52]. A nice example is UGe_2 [53] as, at the first order FM critical pressure $P_c \sim 1.49\,GPa$, the sublattice magnetization

jumps from the FM phase to the PM one from $M_0 = 0.9\,\mu_{\rm B}$ to zero. In zero field, the transition line $T_{\rm Curie}(P)$ between FM and PM changes from second order to first order at a tricriticality point $T_{\rm TCP} \sim 24\,{\rm K}$, $P_{\rm TCP} \sim 1.42\,{\rm GPa}$ [54, 55]. The domain of the first order transition at $H = 0$ is quite narrow $(P_{\rm c} - P_{\rm TCP})/P_{\rm TCP} \sim 0.05$, but recent resistivity measurements [54] as well as thermal expansions [55] data show that FM wings [56] appear under magnetic field, and a first order transition will occur. They will only collapse at $T = 0\,{\rm K}$ for $P > P_{\rm QCEP} \sim 3\,{\rm GPa}$ i. e. $2P_{\rm c}$ around $H_{\rm QCEP} \sim 10\,{\rm T}$. For UGe_2, a large pressure is needed ($2P_{\rm c}$) to reach a PM ground state at any magnetic field (Fig. 10). When the size of the FM sublattice magnetization close to $P_{\rm c}$ decreases, as for UCoGe ($M_0 \sim 0.07\,\mu_{\rm B}$) [57], no detection of FM wings has been reported. Thus the large separation between $P_{\rm QCEP}$ and $P_{\rm c}$ in UGe_2 is clearly linked to the large jump of M_0 at $P_{\rm c}$. Due to the insertion of Yb ions in a cage, one may suspect a very high value of m_B which will furthermore highly vary with the magnetic field.

5. Evidence of $m_{\rm B}$ and m^{**} in FM superconductors

Three U based FM-SC have been discovered, namely UGe_2 [58], URhGe [59], and UCoGe [57]. The respective values of M_0 at $P = 0$ are $1.4\,\mu_{\rm B}$, $0.4\,\mu_{\rm B}$ and $0.07\,\mu_{\rm B}$ and their Curie temperatures $T_{\rm Curie} = 50\,{\rm K}$, $9.5\,{\rm K}$, and $2.8\,{\rm K}$. In UGe_2, SC appears only under pressure with a maximum of the critical SC temperature $T_{\rm SC,max} \sim 0.7\,{\rm K}$ reached close to the pressure $P_{\rm x}$ where the system switches one the ferromagnetic FM2 phase to another ferromagnetic FM1 phase [53]. The discoveries of SC in URhGe ($T_{\rm SC} \sim 0.25\,{\rm K}$) and in UCoGe ($T_{\rm SC} \sim 0.7\,{\rm K}$) already at $P = 0$ open the possibility of careful measurements even at ambient pressure. UGe_2 and UCoGe have a PM ground state above respectively $P_{\rm c} \sim 1.49\,{\rm GPa}$ [53] and $P_{\rm c} \sim 1.2\,{\rm GPa}$ [60, 61, 62], while in URhGe an initial P increase of $T_{\rm Curie}$ is observed, at least up to $P = 13\,{\rm GPa}$ [63]. In contrast to UGe_2, where SC exists only in the FM side, in UCoGe, SC persists also in the PM regime above $P_{\rm c}$. SC in URhGe is suppressed above $p \approx 4\,{\rm GPa}$ [64]. For the low $T_{\rm Curie}$ materials (URhGe [65] and UCoGe [66]), the measurements of the specific heat (see Fig. 11 for URhGe) show clearly the occurrence of a term linear in temperature above $T_{\rm Curie}$ which can be associated to the formation of the renormalized band mass $m_{\rm B}$ already at $T_{\rm Curie}$. Furthermore applying a magnetic field along the easy c axis of magnetization leads to quench the FM fluctuation (thus to the collapse of m_0^{**}) and to restore the sole $m_{\rm B}$ contribution. By contrast, in the high $T_{\rm Curie}$ ($\sim 50\,{\rm K}$) material as UGe_2 [67] there is no mark of renormalized band mass contribution to the specific heat above $T_{\rm Curie}$ at $P = 0$ as its characteristic temperature $T_{\rm B}$ may be quite similar than $T_{\rm Curie}$. The "hidden" character of $m_{\rm B}$ is quite similar to the previous discussion made for $CeRu_2Si_2$.

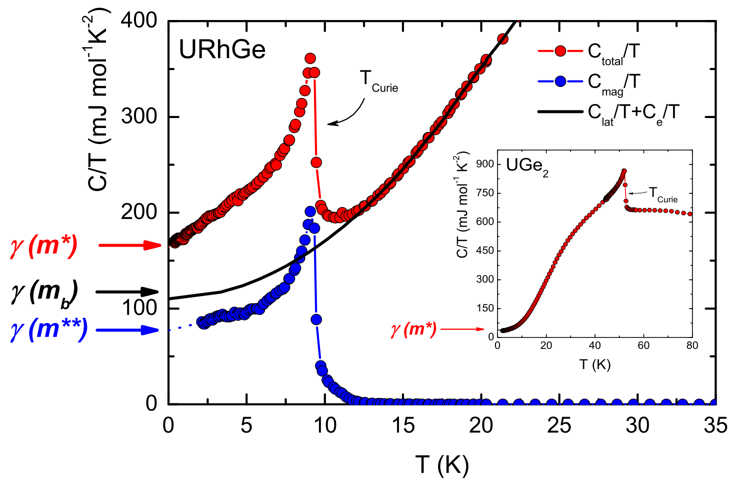


Figure 11. Evidence of the $m_{\rm B}$ strength at ambient pressure for URhGe from the temperature dependence of C/T. The inset shows $C/T(T)$ for UGe_2.

6. Link between m^{**} and T_{SC} in the ferromagnetic superconductor URhGe

URhGe is a very nice example to illustrate the link between the strength of m^{**} and its feedback to SC. A orifinally discovery was that the application of a magnetic field along the b hard-axis induces the re-orientation of the magnetization from the easy c axis to the b axis at a field $H_{\rm R} \sim 12\,{\rm T}$ and this re-orientation is directly associated with a H re-entrance of SC (Fig. 12) [68]. To verify that the driving phenomena is an enhancement of m^{**}, careful resistivity experiments as a function of pressure and magnetic field have been realized [64, 69]. Furthermore, this coupling was verified by detailed magnetization (M) studies. Figure 13 compares the field enhancement of $\Delta m^*/m^*$ detected by resistivity (ρ) and magnetization [70]. Taking into account that magnetization measurements are limited down to $T = 1.5$ K while resistivity has been realized down to $70\,mK$, the agreement can be considered excellent. Assuming that the H enhancement of m^* is that of m_0^{**}, via the McMillan-type formula $T_{\rm SC}(m^*) = T_0 \exp(-m^*/m^{**})$, the field re-entrance (RCS) of SC as well as its collapse at a pressure $P_{\rm RSC} \sim 2\,{\rm GPa}$, which is two times smaller than the pressure $P_{\rm LFSC} \sim 4\,{\rm GPa}$ where SC would collapse in a low field, were quantitatively explained. To our knowledge, it is the first case where a link between the mass enhancement and the appearance of SC has been shown successfully on a given material between the (P, H) variation of m^{**} and of $T_{\rm SC}(m^{**})$.

An anomalous temperature dependence of the upper critical field $H_{c2}(T)$ has also been reported in UCoGe when the field is applied perpendicular to the easy c axis [71]. The common point with URhGe is that in this Ising type ferromagnet when H is applied along the hard magnetization axis (see [70]) the Curie temperature decreases with H,

as proofed theoretically [72], which will obviously lead to field mass enhancement. In UCoGe, there is no evidence that the anomalies of H_{c2} for field perpendicular to the c

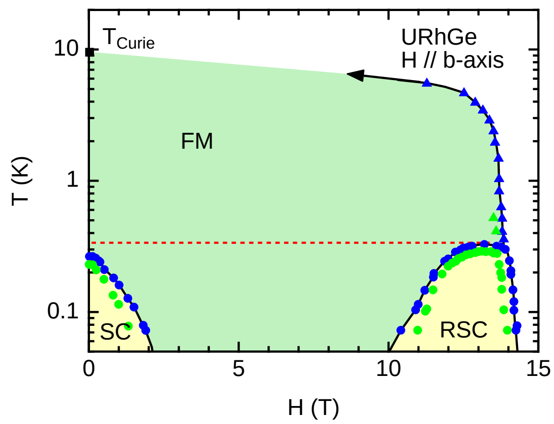


Figure 12. H, T phase diagram of URhGe at ambient pressure with the occurrence of low field SC and H reentrant superconductivity at H_R which is directly associated with the field mass enhancement (see [68, 69]).

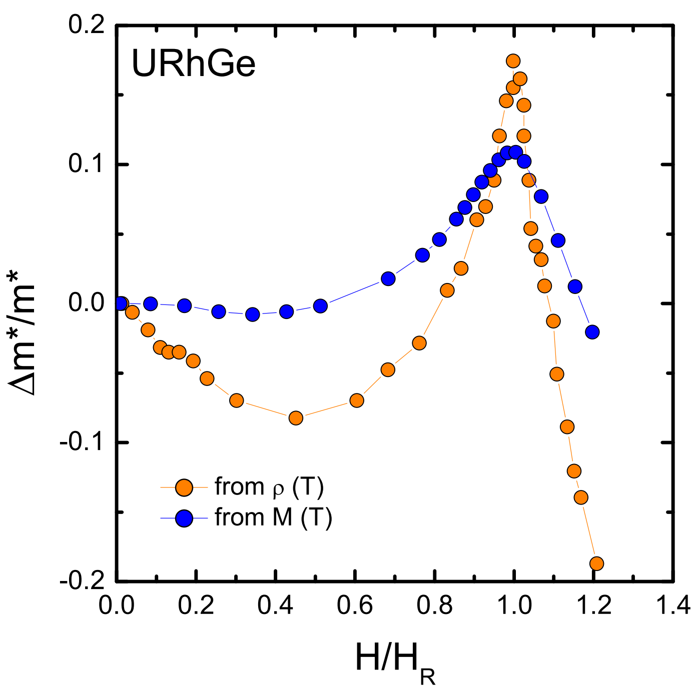


Figure 13. H enhancement of the effective mass as deduced from the A coefficient of the resistivity measurements down to 80 mK and from the temperature dependence of magnetization measurements down 1.5 K using the Maxwell relation [65].

axis is correlated with a spin re-orientation. The key parameter may be the size of the field induced moment for example $\chi_b H$ (χ_b is the susceptibility along the hard b axis) by comparison to M_0. It will drive the spin re-orientation if χ_b is greater than χ_c as it is the case for URhGe. Any induced supplementary component along the c axis via an angular misalignment of the b axis versus the magnetic field direction will wipe out rapidly the phenomena as an extra magnetic component along c leads to the opposite to a decrease of the strength of the spin fluctuations. Recently a theory on field induced Ising spin fluctuations has been developed [73].

7. Interplay of antiferromagnetism and superconductivity: before and after the discovery of 115 compounds

Careful studies on the interplay between AF and SC were quite limited before the appearance of the Ce-115 HFC as the SC dome near P_c occurs at low temperature ($T = 0.6\,\mathrm{K}$ or lower) far below the maximum of the Néel temperature ($T_{\mathrm{N,max}}$) of the AF transition. The discovery of SC in Ce-115 compounds (discussed by T. Parks at this conference) opens new opportunities to study in detaile the interplay of AF and SC, notably on the $CeRhIn_5$, via resistivity, microcalorimetry, and neutron scattering as both transition temperatures are comparable. Figure 14 represents the (T, P, H) phase diagram of $CeRhIn_5$ determined in Grenoble [22, 74].

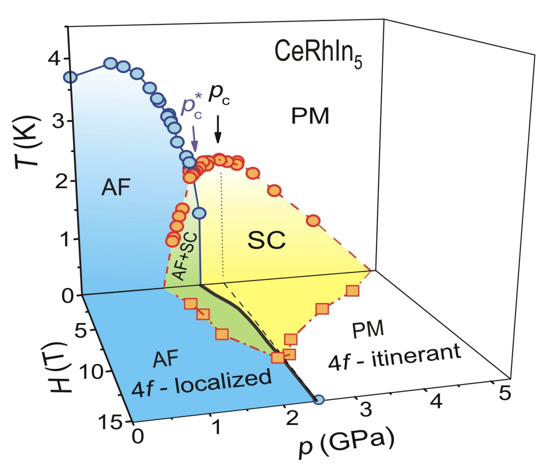
The main point is that at $H = 0$, above $P = P_c^* \approx 2\,\mathrm{GPa}$ where $T_{\mathrm{SC}} = T_\mathrm{N}(P = P_\mathrm{c}^*)$, the opening of a large SC gap leads to the rapid suppression of antiferromagnetism at $P = P_\mathrm{c}^* + \varepsilon$. However, in absence of SC, AF will survive up to $P_\mathrm{c} \sim 2.5\,\mathrm{GPa}$. From macroscopic measurements [22, 74, 75], the coexisting domain of AF + SC is small with the onset of SC at $P_\mathrm{S}^+ \sim 1.5\,\mathrm{GPa}$ and a disappearance of AF close to P_c^*. Looking only to the specific heat anomaly at the phase transition from the AF phase to the AF + SC state indicates that the transition is not at all BCS like. NMR experiment give two piece of evidence [76] that (i) the ground state appear homogeneous i. e. with no phase separation between AF and SC components, (ii) the magnetic structure switches from incommensurate to commensurate.

The striking new phenomena in magnetic field is the lowering of the strength of SC and the creation of vortices. Both phenomena lead to the H re-entrance of AF to occur up to the pressure P_c [22, 74, 75]. Up to now, no microscopic studies have been realized in the high magnetic field AF + SC phase. As indicated on Fig. 14, two clear limits exist: (i) the low pressure $P < P_\mathrm{s}^+ = 1.5\,\mathrm{GPa}$ regime, where only AF occurs, the Fermi surface corresponds to a local behavior of the 4f electron, (ii) the high pressure limit with $P > P_\mathrm{c}$, where a pure SC phase exists up to H_{c2} and the Fermi surface implies an itinerant character of the 4f electrons [77]. Between P_s^+ and P_c for $H < H_{\mathrm{c2}}$, the FS must evolve in pressure and magnetic field between the AF + SC phase and the pure SC phase.

The $(H, P, T = 0\,\mathrm{K})$ phase diagram of $CeRhIn_5$ is quite analogous to that proposed for the high T_c superconductors (e.g. $YBa_2Cu_3O_{7-x}$) with the change from spin density

wave insulator to SC + spin density wave with small Fermi surface pockets and then ending to a pure SC phase with "normal" large Fermi Surface [78] as a function of the hole concentration. Thanks to the recent discoveries of new SC materials such as the pnictides, e.g.(see [79]) there are now many examples of an interplay between AF and SC with the occurrence of either an homogeneous phase or a phase separation. Precise experiments can be realized in future to reach a clearer view.

$CeCoIn_5$ corresponds to the case of a pure SC phase at ambient pressure. A consequence of the previous remarks that high magnetic polarization can be reached plus the weakness of the Pauli limit of $H_{c2}(0)$ with respect to the orbital one pushes the interpretation of the appearance of a new high magnetic field low temperature phase (HFLT) to be a FFLO phase [80, 81] as predicted four decades ago by Fulde-Ferrel [82] and Larkin-Ovchinnikov [83]. However recent NMR [84, 85] and neutron scattering experiments [86, 87] for $H \parallel a$ prove clearly that the HFLT phase has a long range magnetic component and the wave vector does not change with the direction of the magnetic field. Here, we will not discuss in detail the physics of the HFLT, but recently we have realized a new set of magnetization experiments with $H \parallel c$ in order to clarify whether exactly at $H_{c2}(0)$ a quantum singularity exists since the $H_{c2}(0)$ point is not associated with a magnetic quantum criticality [88]. Our magnetization ($M(H)$) measurements performed down to 80 mK are mainly an improvement by a fine zoom in the $(H - H_{c2})/H_{c2}$ window of previous published data [89]. Figure 15 shows at constant field value, the temperature variation of $M(H,T)$. This spectacular result is that, below $H_{c2}(0)$, $M(T)$ approaches a T^2 dependence with a T decrease of $M(H)$ on cooling while above $H_{c2}(0)$, $M(H,T)$ does not obey a T^2 Fermi liquid law but a quasi linear T dependence with an increase of $M(H)$ on cooling. Using Maxwell relations it can be clearly shown that coming from the SC phase a sharp maxima of the γ term of the specific heat will occur at $H_{c2}(0)$. The extrapolation of the suspected divergence



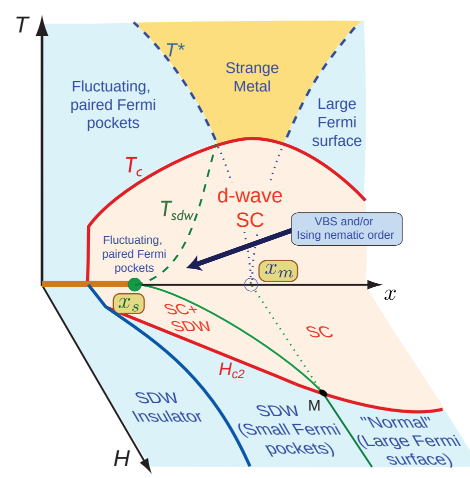


Figure 14. (H, T, P) phase diagram of $CeRhIn_5$ compared to the one proposed for the high T_c superconductor [77, 78].

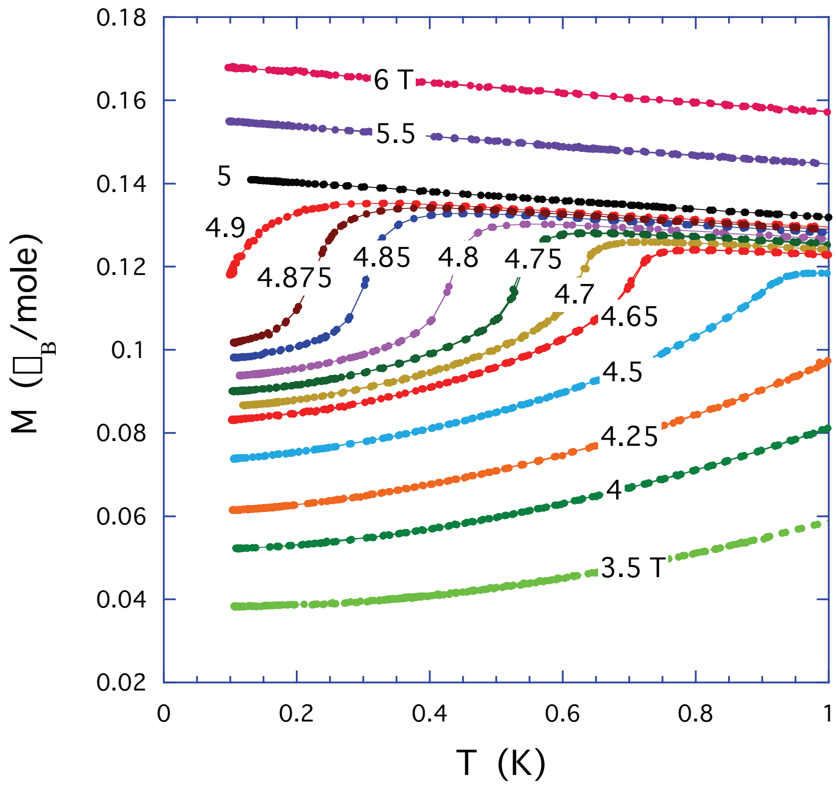


Figure 15. Magnetization as function of temperature at constant field $H \parallel c$ of $CeCoIn_5$ showing clearly the singular magnetic behaviour right at H_{c2}.

of the effective mass from the field dependence of the A coefficient of the resistivity measured at fields above $H_{c2}(0)$ at $H_{QCP} \sim 4.3$ T [90] is not marked by any change of the field dependence of the $\gamma(H)$ at H_{QCP}. Experimentally it should be possible to push down the magnetization measurements below 20 mK where a Fermi liquid temperature dependence of M may be obeyed on both sides of $H_{c2}(0)$ and to establish if at $H_{c2}(0)$ the field dependence of γ has no discontinuity linked to the first order nature of the transition. The unusual behavior, notably the quasi linear T variation of M above $H_{c2}(0)$ at least down to 80 mK is a consequence of the interference between magnetic fluctuations and superconducting correlations as also discussed recently in organic and pnictide superconductors [91]. Thus, there is a clear evidence that $H_{c2}(0)$ is a quantum singularity caused by the interplay of normal and superconducting properties. It was proved that AF criticality can be induced by the onset of superconductivity around $H_{c2}(0)$ [92]. The exciting phenomena in $CeCoIn_5$ is that magnetism is glued to SC as if the H weakening of the SC gaps leads to a restoration of a pseudogap structure favorable to AF. Even more the first order magnetization jump is quite similar macroscopically to the metamagnetic phenomena described previously for the $CeRu_2Si_2$ series. It has been proposed that the tendency of field induced AF ordering is linked to strong Pauli depairing (as can be viewed for pseudometamagnetism) and strongly favored by unconventional SC gap node along the AF modulation [93]. The localisation

of a magnetic quantum critical point in the (H, T, P) phase diagram of $CeCoIn_5$ in the absence of SC is still an open question. At least, the absence of H re-entrant AF above $H_{c2}(0)$ for any field direction implies that the magnetic critical field at $P = 0$ will be lower than $H_{c2}(0)$ and already at ambient pressure $CeCoIn_5$ is above $P_c^\star$ [34].

8. The hidden order phase of URu_2Si_2: feedback between FS instability and spin dynamics

Attempts to resolve the nature of the hidden order phase of URu_2Si_2 boosts an intense experimental and theoretical activity over the last decade (see [94]). As several invited contributions (J. C. Davis, P. M. Oppeneer, and H. Harima (see [95, 96, 97]) have treated this problem, we will stress only a few points. One of the paradox of URu_2Si_2 represented in Fig. 16 is that above its ordering temperature $T_0 \sim 17.5\,\mathrm{K}$, it looks as a classical intermediate valence compound with e.g. a broad maximum of C/T as observed for $CeSn_3$ [98]. Knowing the entropy involved at low temperature, without any phase transition at T_0, its residual γ term would be around $100\,\mathrm{mJ\,mole^{-1}K^{-2}}$ and a smooth continuous decrease of C/T will occur on cooling. However the phase transition at T_0 is associated with a drastic change leading to a marked increase of C/T on cooling as observed for usual HFC [99]. Low energy must be involved as the temperature variation of the Grüneisen coefficient is large on cooling [100].

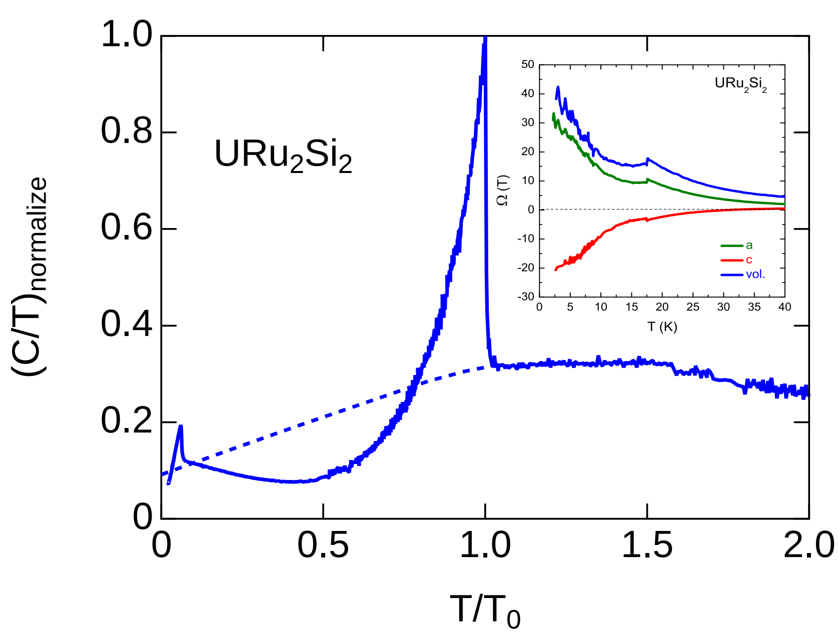


Figure 16. Temperature dependence of normalized specific heat for URu_2Si_2 (full line). The dashed line indicates an extrapolation below T_0 of C/T assuming the survival of PM state. The insert shows the T dependence of the Grüneisen coefficient [98].

It is now well established by transport measurements (Hall effect, Nernst effect, thermoelectric power) (see [94, 98]), by NMR [101], high energy spectroscopy [102]

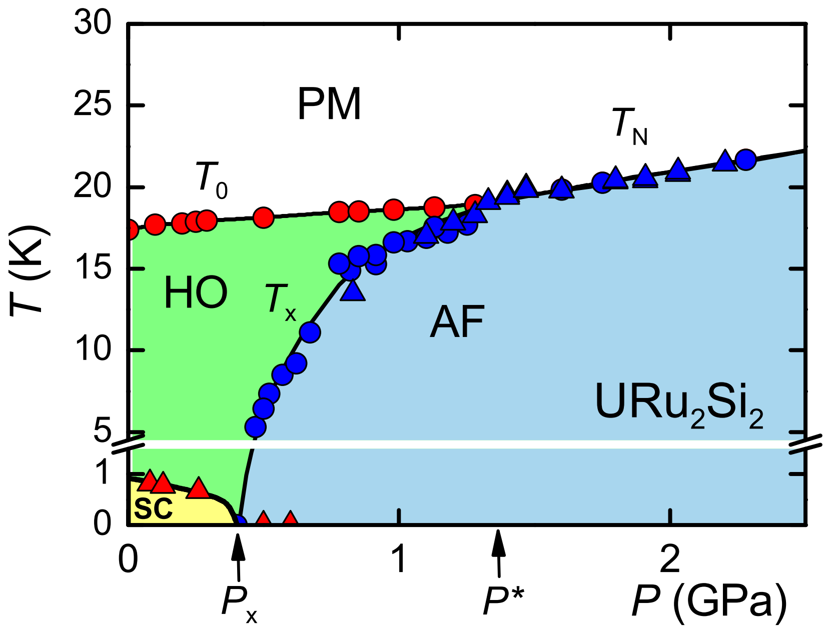


Figure 17. (T, P) phase diagram of URu_2Si_2 with the location of the PM, HO and HF boundaries. SC exists only in the HO phase i. e. below P_x. AF, HO and PM meets at the initial pressure P^* [104].

and recently by two scanning tunneling microscope observations [95, 103] that a Fermi surface reconstruction must occur below T_0 going from PM to HO states. The (P, H, T) phase diagram of URu_2Si_2 (Fig. 17) [104, 105] is now well established despite qualitative differences coming from the high sensitivity of the system to pressure inhomogeneity. The observation of an inelastic excitation at wave vector $Q_0 = (1, 0, 0)$ by inelastic neutron scattering experiments in the HO phase at the same wave vector [106] where AF is detected at high pressure via strong elastic neutron reflection and the strong similarity [107, 108] in the dHvA frequencies detected for both HO and AF ground states are in strong support of the idea that both phases must have the same wave vector $(0, 0, 1)$ implying a doubling of the lattice along c. This conclusion is reinforced by recent low energy ARPES measurements reported in this conference [109]. The idea is that at T_0, a Fermi Surface reconstruction occurs going from body center tetragonal space group #139 above T_0 to a simple tetragonal either #136 or #123 (see reference [97, 96]). The persistence inside the tetragonal symmetry is in full agreement with STM data. The change of tetragonal space group is associated with a gap opening of characteristic energy Δ_G; the drop of carrier density has a direct feedback on the spin dynamics (development of sharp excitation at $Q_0 = (1, 0, 0)$ and $Q_1 = (0.6, 0, 0)$) which may open the possibility that the U centers even in an intermediate valence phase may have their multipolar properties renormalized to the U^{4+} configuration see [96]). Thus quadrupole [97] or hexadecapole [110] are invoked for the OP of URu_2Si_2. It is even proposed that the HO phase may be still a PM state with a lattice switch from space group #139 to #123 [96] with a gap opening in the HO phase generated by

the strong dynamical longitudinal Ising type magnetic fluctuation induced along the c axis. An incommensurate spin density wave was proposed in association with the existence of sharp excitations at $Q_1 = (0.6, 0, 0)$ [111], however there is no evidence of any associated detectable OP in neutron scatterings X-ray or STM. Despite many attempts the puzzle of the HO is not resolved. For example, up to now all aims to detect quadrupole or hexadecapole ordering by X-ray methods at synchrotron beam have failed. Recently, careful designed uniaxial strain neutron scattering experiments on URu_2Si_2 [112] indicate that HO and AF cannot be mixed when the strain is applied in the basal plane. This result supports strongly the absence of time reversal breaking in HO opposite to the case of AF. Definitively, strong progress has been made but the final solution on the hidden order is not given. Thus still different theoretical proposals are made and experimentalists dream to find the solution.

9. The Future: Material, Instrumentation, Experiments

9.1. Material

The main new trends are often associated with the discovery of unexpected effects on new material. In the last decade, we can quote for HFC:

- the ferromagnetic superconductor,
- the appearance of Ce115 series,
- the SC in compounds with non-centrosymmetric crystal structure (see E. Bauer this conference),
- the criticality of Yb compounds ($YbRh_2Si_2$, $\beta YbAlB_4$) and recently YbT_2Zn_{20} series.

Even on well defined physical problems such as SC of FM HFC it is crucial to find a case at ambient pressure where clean crystals can be grown enabling deep studies on up-up and down-down spin component. For Yb HFC, the priority is to find an example with high critical field singularities (H_c) allowing unambiguously the determination of the Fermi Surface instability.

9.2. Instrumentation

Major progresses have been in experiments in extreme conditions (very low temperature, high pressure, high magnetic fields) which allow large scans for the (H, P, T) determination of phase diagram. Important breakthroughs have been made in the determination of basic quantities such as specific heat, thermal expansion (via strain gauge, Larmor precession), and NMR. High energy spectroscopy can now be realized at low temperature ($T \sim 4\,\mathrm{K}$) with excellent resolutions. STM will certainly be able to give new insights on electronic structures related either with intrinsic properties or extrinsic properties correlated with specific defects. One hope is that fancy superstructures or intrinsic defects maybe discovered associated with the strong pressure and uniaxial strain

dependence of materials near quantum singularities. At least, it is clear that all this improvements already play an important role in determining the HO state of URu_2Si_2.

9.3. Physical problems

Precise determination of H, P, T phase diagram is a first key goal as studies on Ce-115 HFC or URu_2Si_2 have shown. For example, in ferromagnetic superconductors such as UGe_2, it is not clear what is the thermodynamic boundary of SC inside the FM phases and notably, if SC can occur homogeneously inside the low pressure large sublattice magnetization phase FM2. To give a definite answer the combination of experiments with different probes are absolutely necessary.

An interesting field is the polarized paramagnetic phase which can be obtained through a metamagnetic or pseudo-metamagnetic transition. However the full experimental determination of the Fermi surface has never been achieved. For example, for $CeRu_2Si_2$ above H_M, a large part of the Fermi surface is still missing. To resolve this enigma is a challenging goal. A new emerging phenomena is the occurrence of 2.5 Lifshiftz instability directly associated with the large magnetic polarization induced by the magnetic field (two cases have been pointed out $CeIn_3$ [113] and URu_2Si_2 [114].

The detection of other exotic phases such as multipolar ordering [115], Pomeranchuk instability, nematic phases, Kondo topological insulator [116] requires the exploration of a large domain. Systematic studies on skutterudite materials have pointed out quite new cases such as $PrFe_4P_{12}$ [117]. In unconventional SC, we have already stressed the interest to precisely determine the properties of the AF + SC phases. For FM-SC, it is quite obvious that spontaneous vortices must occur as the internal field produced by the magnetization surpasses often the first superconducting critical field $H_{c1}(0)$. However, up to now a clear observation of spontaneous vortices have not been achieved [118]. Another interesting question concerns (e.g. UCoGe) the possible occurrence of SC on both side of P_c may lead to a change in the phases near P_c [119]. In most HFC-SC, the origin of SC is considered to be mediated through magnetic, valence fluctuations or mixed effects of both phenomena. In exotic cases like URu_2Si_2 or $PrOs_4Sb_{12}$ [120], SC is associated to the HO phase and to the proximity to a multipolar instability, respectively. To clarify their SC singularities with respect to the previous examples is also a stimulating goal.

To stress that many problems remain to be revisited (see [18]), let us indicate that for example, the classification of $CeAl_3$ as a canonical example of PM Kondo lattice is quite controversial as (i) in single crystals a clear AF anomaly has been observed [121, 122] and (ii) microscopic measurements (as muon spectroscopy presented here [123]) confirm that a long range magnetic component exists at $P = 0$. These points agree with a negative sign of the thermal expansion indicating that quantum singularity must occur at a slightly higher pressure ($P_\mathrm{c} \sim 0.2\,\mathrm{GPa}$, $H_\mathrm{c} \sim 2\,\mathrm{T}$) than at ambient pressure. For the archetype strong coupling HFC UBe_{13}, there is strong evidence that P and H are carrier "pumps" [18] and thus lead to a continuous change of the zero

field SC reference. One can speculate that a magnetic field breaks the cubic symmetry leading to a drastic change of the FS with H. This hypothesis have to be tested by modeling band structure calculations with magnetostriction data. Even for the double transition of UPt_3, the origin of the postulated symmetry breaking field by AF remains unclear as the origin of the tiny ordered moment observed only in neutron scattering experiments is far being fully understood.

Thus, depending on the level of understanding, the HFC are challenging materials with properties which have strong impact on other strongly correlated electronic materials going from organic conductors, high T_c SC, recent pnictides, and 3d transition metals.

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